CATALYTIC PRODUCTION OF FURFURAL BY THE SUBCRITICAL HYDROTHERMAL GASIFICATION OF FLAX STRAW

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By
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Laila Ibrahim Jaafari, candidate for the degree of Master of Applied Science in Process Systems Engineering, has presented a thesis titled, *Catalytic Production of Furfural by the Subcritical Hydrothermal Gasification of Flax Straw*, in an oral examination held on December 12, 2013. The following committee members have found the thesis acceptable in form and content, and that the candidate demonstrated satisfactory knowledge of the subject material.

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ABSTRACT

Developing new sources of energy that can mitigate greenhouse gas (GHG) emissions has generated a strong research interest in the past two decades. Renewable sources of energy have become strong candidates for replacing the conventional resources in order to ameliorate the high level of pollution caused by the use of conventional fossil fuels. Biomass is a type of renewable resource that is considered to be carbon neutral when used in producing fuels and chemicals. Flax straw is an example of biomass that accumulates in Canada in high amounts. It is difficult to dispose of because it does not decompose easily as a result of its tough fibrous nature. However, it can be used through a hydrothermal gasification process to produce gaseous fuels as well as some important liquid products. Hydrothermal gasification process was used in this research because it can deal with wet biomass without the necessity of the drying step. Furfural is an important chemical that has many industrial applications, and as such, was considered to be the major desired product through the hydrothermal gasification of flax straw using a solid acid catalyst.

This study focused on the catalytic subcritical hydrothermal gasification of flax straw. The study was performed using a 600 mL autoclave batch reactor using flax straw with a fixed weight (10 g) in all the experimental runs. Three types of solid acid catalysts were explored in this study: γ–alumina, H-ZSM-5, and silica-alumina. Experimental parameters such as temperature (200-325 °C), pressure (0-60 bar), residence time (0-120 min) and weight of solid acid catalysts (0.5-1.5 g) were varied in order to obtain the optimum conditions and to select the best catalyst for producing furfural.
The yields of both gas and phenol were also monitored in the study. The yield of gas was quantified using an online gas chromatograph (GC). The gas products included hydrogen ($H_2$), carbon monoxide (CO), carbon dioxide ($CO_2$) and trace amounts of methane ($CH_4$) and ethane ($C_2H_6$). The yields of furfural and phenol were measured by gas chromatograph/mass spectrometer (GC/MS). The results showed that the production of furfural was affected by all the experimental parameters (temperature, pressure, residence time and weight of the solid acid catalysts). The highest yield of furfural was obtained using $\gamma$-alumina with 0.1 g as the optimum weight of catalyst per g of flax straw. The ranking of the three catalysts based on furfural production was: $\gamma$–alumina > H-ZSM-5 > silica-alumina. This had a direct correlation with the ratio of Lewis to Brønsted acid sites which decreased similar to the ranking of the performance of the catalysts.

A kinetic study of the catalytic subcritical hydrothermal gasification of flax straw using 1 g of $\gamma$–alumina was also performed. Kinetic data were obtained using 10 g of flax straw, autogenous pressure, temperatures in the range of 225-325 °C, and residence time in the range of 0-120 min. The data were analysed using an empirical power law rate model. The carbon conversion was calculated using the ultimate analysis, which gave the highest conversion of 66% at 325 °C compared to the conversion of 40% obtained for a previous non-catalytic study.

The final kinetic model was: 

$$-r_A = \frac{dX_A}{dt} = 7.038 \times 10^{-2} e^{-9463.5/R*T} (1 - X_A)^2.$$

The activation energy achieved in this study was lower than the activation energy of 27,969.6 J/mol obtained by the non-catalytic study thus showing the importance of the catalyst in lowering the energy barrier. The predicted rates from the model showed good agreement with the experimental rates with an average absolute deviation of 8.6%.
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NOMENCLATURE AND ABBREVIATIONS

T: Temperature

\( \text{CH}_{1.5}\text{O}_{0.62} \): Formula of Flax Straw

K: Degree Kalvin

\( ^\circ \text{C} \): Degree Celsius

AAD: Average Absolute Deviation

\%: Percent.

\( \text{CO}_2 \): Carbon Dioxide

\( \text{CO} \): Carbon Monoxide

\( \text{H}_2 \): Hydrogen

A: Collision or Pre-exponential Factor

J: Joule

n: Reaction order

\( \text{N}_2 \): Nitrogen

g: Gram

\( \text{C}_6\text{H}_5\text{OH} \): Phenol

\( \text{C}_5\text{H}_4\text{O}_2 \): Furfural

\( \text{OH}^- \): Hydroxide ion
\[ \text{O}_2: \quad \text{Oxygen} \]

\[ \text{MPa:} \quad \text{Mega Pascal} \]

\[ \text{mL:} \quad \text{Millilitre} \]

\[ \text{mm:} \quad \text{Millimetre} \]

\[ t: \quad \text{Reaction time} \]

\[ \text{min:} \quad \text{Minutes} \]

\[ \text{mg:} \quad \text{Milligram} \]

\[ \text{w\%:} \quad \text{Weight Percent} \]

\[ k: \quad \text{Rate constant} \]

\[ \text{i.d:} \quad \text{Internal diameter} \]

\[ \text{NLREG:} \quad \text{Non-Linear Regression} \]

\[ \text{P:} \quad \text{Pressure} \]

\[ \text{bar:} \quad \text{Pressure Unit} \]

\[ \text{C}_2\text{H}_5: \quad \text{Ethane} \]

\[ \text{CH}_4: \quad \text{Methane} \]

\[ \text{C}_6\text{H}_{12}\text{O}_6: \quad \text{Glucose} \]

\[ \text{H}^+: \quad \text{Hydrogen ion} \]

\[ \text{H}_2\text{O}: \quad \text{Water} \]
H-ZSM-5: Zeolite catalyst

GC/MS: Gas Chromatogram/Mass Spectroscopy

GC: Gas Chromatogram

Ea: Activation Energy

R: Molar gas constant (8.314 J/mol/K)

CHNS: Carbon-Hydrogen-Nitrogen-Sulphur

Psi: Pounds per square inch

Xc: carbon conversion

Wci: weight of the carbon in flax straw

We: weight of carbon in char at the end of reaction
CHAPTER 1
INTRODUCTION AND BACKGROUND

1.1 BIOMASS AND RENEWABLE ENERGY SOURCES

Developing alternative and renewable sources of energy has received considerable interest because of the strong need to mitigate the high amounts of greenhouse gases (GHGs) produced from the use of conventional fossil fuel sources. The interest in renewable sources of energy arises because they are considered to be sustainable, hazard free, safe and environmentally friendly (Tushar, 2010). Currently, the dominant resource for energy production is fossil fuel compared with the very low usage of renewable energy sources. Figure 1.1 shows the contribution of fossil fuels and renewable sources in the energy portfolio. The consumptions of fossil fuels, namely, oil, natural gas and coal account for 30%, 22% and 28%, respectively for a total of 80% whereas the consumption of renewable sources accounts only for 17% (Friday, 2013). This makes it necessary to increase the contribution of renewable resources to the energy portfolio if we are to significantly lower GHG emissions. Biomass is an example of a renewable source of energy, which generally can be described as any product extracted from animals or vegetable sources. According to Brunner (2009), biomass can be used as a raw material to produce useful chemicals as well as for producing energy. It is also known that biomass is a safe source of energy and can be used to decrease the emissions of the hazardous gases such as SO\textsubscript{x} and NO\textsubscript{x} as well as GHGs (Pastircakova, 2004). Economically, it is known that biomass is available everywhere and that makes it less expensive than conventional energy sources. The main interest has been to increase the use of lignocellulosic biomass to produce new sources of energy (Kumar, 2010).
Figure 1.1: The total final energy use (Friday, 2013)
1.2 BASIC CONTENTS OF BIOMASS

In general, biomass consists of cellulose, hemi-cellulose and lignin. Fig.1.2 shows the percentages of the basic contents of biomass (Kumar, 2010). The presence of these three polymeric contents in plants increases their strength and solidity. Cellulose is the major component in plants, which can produce oligomer and monomer sugars by the hydrolysis process at high pressures (Sasaki et al., 1998). According to Brunner (2009) the hydrolysis of cellulose produces glucose and oligomers, which can be transformed to form gas, char and oil. Cellulose mainly consists of anhydrous glucose in a chain structure. The molecules of anhydroglucose are linked by β- glycosidic in a chain of linear structure, which increases the stability of cellulose. The importance of cellulose is to provide the solidity of the plant. The second major component in plants is hemicellulose, which consists of side chains of different sugars in a polymer structure. According to Bobleter (1994), these sugars could be classified either as five carbons (arabinose, and xylose) or six carbons (glucose, mannose, galactose). The hemicellulose works as glue for the cellulose units through hydrogen bonds.

The third major component in plants is lignin, which is one of the complex components present in the plants. Lignin consists mainly of different units of phenyl propane as sinapyl alcohol, p- cocumaryl alcohol, and coniferyl alcohol. Lignin works as a linkage for the plant cellular and as protector against chemical or microorganism effects. In addition, lignin is the controller of the fluid flow through plants and it can work as an antioxidant because it absorbs UV lights (Meister, 1996; Olsson, et al., 2005; Falkehag, 1975).
Figure 1.2: The main lignocellulosic biomass composition (Kumar, 2010).
1.3 SCOPE OF THE THESIS

The economy of Saskatchewan depends to a large extent on the agricultural sector (Tusher, 2010). It has been mentioned that the production of flax in Saskatchewan represents 70% of the world production (Comeau, 2006). The production of flax generates high amounts of flax straw. Flax straw has a strong fiber, which needs a long time to breakdown in the soil. Farmers are challenged by the high accumulation of flax straw after harvest. One possible solution is burning the flax straw to decrease accumulation. However, it has been suggested that the better solution is to find methods to use the flax straw as a valuable source for producing useful chemicals (Agriculture and Agric-Food Canada, 2011).

Subcritical hydrothermal gasification of flax straw is a good choice to produce liquid products. The properties of Water at subcritical condition play an important role in converting the organic biomass to produce chemicals and fuels. Hydrothermal gasification of biomass at subcritical water provides renewable sources of energy that could decrease the dependence on the conventional fossil fuels. Flax straw can be used to produce liquid products such as furfural, aldehydes, acids, etc. (Juben et al., 2007). The production of Furfural is the objective of this study. Furfural is produced through an ionic pathway, which can be accelerated at subcritical water conditions. Furfural is one of the important organic compounds in industrial (Huber et al., 2006). In this study different solid acid catalysts have been used to investigate their effect on increasing the furfural yield.
1.4 RESEARCH OBJECTIVES

The main objective of this study is investigating the performance of the solid acid catalysts on the furfural production through hydrothermal gasification of flax straw in subcritical water conditions. The objectives of this study are listed below:

- Selecting the solid acid catalyst that could increase furfural yield.
- Determining the optimum temperature for furfural production.
- Determining the optimum pressure for increasing liquid yield while decreasing gas yield.
- Performing characterization analysis for the catalysts to interpret their performance in furfural production in relation to their characteristics.
- Obtaining higher carbon conversion at a lower activation energy compared with the non-catalytic process.
- Developing an empirical rate model to interpret the kinetics of the catalytic subcritical hydrothermal gasification of flax straw.
CHAPTER 2

LITERATURE REVIEW

This chapter will focus on reviewing the literature review pertinent to the hydrothermal gasification of vegetable biomass. The advantages of the hydrothermal gasification process over the conventional thermal processes will be reviewed. This chapter will also highlight the importance of water as a reactant in the hydrothermal gasification process. Moreover, the properties of water in sub/supercritical conditions will be explained to show the contribution of water in the hydrothermal gasification process. The production of furfural using liquid acid catalysts will be covered in this section to indicate the necessity of using solid acid catalysts for the hydrothermal gasification process.

2.1 TECHNOLOGIES USED TO PROCESS THE BIOMASS

The technologies used for gasification of biomass are categorised as either thermal or hydrothermal processes. In thermal methods such as pyrolysis or partial oxidation, the biomass must be dried to less than 10wt% of moisture content. Since most biomass resources have a high amount of moisture (> 50wt%), this leads to a high consumption of energy during the drying process. On the other hand, hydrothermal gasification is a process that does not require dry biomass and can be applied to biomass of high moisture content (Elliott, 2008).
2.2 HYDROTHERMAL GASIFICATION OF BIOMASS

Hydrothermal gasification of biomass has been defined as a process that uses water as a reaction medium (Kruse and Dinjus, 2007). This process can be performed at subcritical or supercritical conditions of water. According to Kruse (2009), hydrothermal gasification has advantages over thermal processes, because the presence of water in the former leads to the inhibition of tar and coke formation. The dilution of the reactive contents of the biomass in water reduces polymerization reactions, which in turn, decreases the rate of tar and coke formation. Furthermore, the gasification of biomass can occur at temperatures lower than those of the thermal processes. This project focused on hydrothermal gasification at subcritical water condition, which is highly advantageous because of its low operational temperature compared with the supercritical water process. Subcritical water condition helps to increase the yields of the liquid products more than those of the gas products because of the unique water properties in this region. This increases the solubility of the organic material present in the biomass. Water at subcritical conditions, especially near to the critical temperature, becomes suitable for extracting non-polar compounds such as hydrocarbons and metals because water has a low polarity at this condition (Kronholm et al, 2002; Brunner et al., 2001). In the hydrothermal gasification process water participates as a solvent, reactant and catalyst simultaneously. The contribution of water in this process saves the cost of the drying process. The hydrolysis reaction becomes faster at sub or supercritical conditions of water leading to a high degradation of the biomass. Many researchers have studied the hydrothermal gasification of biomass as presented below in the literature review about the process.
Minowa et al. (1998; 1999) studied the hydrothermal gasification of cellulose at temperatures ranging from 200 - 350°C and a pressure of 20 Mpa (200 bar). The experiments were performed with and without catalyst at a reaction time up to 60 minutes. The researchers investigated the effects of different supported nickel and alkali catalysts on the reaction products in an autoclave reactor. The hydrolysis process led to the formation of glucose and oligomers, which decomposed to form gases, aqueous phase, oil and char. However, the alkali catalyst was found to inhibit char formation. The use of Ni metal catalyzed steam reforming and methanation reactions. The main gas products were CO₂, H₂ and CH₄, and the highest yields of H₂ and CO₂ were obtained at 350°C; however, increasing the reaction time decreased the yield of the two gases. The activity of the different catalyst supports affected the gas yield.

In a different study, Fang et al. (2004) examined the decomposition of cellulose with and without catalyst. The study was performed using an autoclave reactor and a micro reactor each at 350 °C. Two types of catalysts were used: Na₂CO₃ and Ni. The results showed that a solid residue was the main product in the non-catalytic experiment. On the other hand, the catalyst increased the gas and oil product yields. The reaction was performed under heterogeneous and homogeneous phases. Waldner and Vogel (2005) investigated the hydrothermal gasification of wood at sub/supercritical conditions of water in the presence of a catalyst. A batch reactor was used with a feed concentration of 10-30 wt %. Raney nickel catalyst was used in this study at a temperature range from 300-410°C and pressure range of 12-34 Mpa (120- 340 bar). The investigation showed that the efficiency of carbon gasification was a function of the time of the reaction up to 90 minutes. The methane yield was found to be 0.33 (g CH₄/g
wood). However, at the supercritical condition, there was no tar formation. The liquefaction of the wood produced D-glucose, alcohols, formic acid and 5-hydroxymethylfurfural (5-HMF).

Hashaikeh et al. (2006) studied the catalytic effect on the hydrothermal gasification of glucose with (0.1-1M) concentration to form CH₄, CO₂, and H₂. The experiments were carried out in a diamond – anvil cell and continuous – flow reactors at a temperature range of 238- 250°C and a pressure of 10 Mpa (100 bar). Pt/Al₂O₃ catalyst was used in this study. The results showed that 5-HMF was formed because of the dehydration of glucose; however, using a high concentration of glucose (above 1M) clogged the reactor. Fang et al. (2008) studied the hydrothermal gasification of cellulose and glucose with a heterogeneous catalyst. The experiments were conducted in an autoclave, flow, and micro reactors with a pressure of 30 Mpa (300 bar) and different residence time up to 60 minutes. As a result, Pt catalyst was found to be more active compared to Ru and Ni. Using Ni with cellulose in the autoclave gave a low gasification rate but by using Ni/ silica-alumina at 350°C and 30 min, the gasification rate was 96 wt%. On the other hand, using Pt-γ-alumina for hydrothermal gasification of glucose at 360°C and 30 Mpa (300 bar) achieved 67wt % of gasification rate with 44 mole % of hydrogen yield.

Azadi et al. (2009) have discussed the effect of using catalyst on the hydrothermal gasification of model compounds of biomass such as glucose under subcritical water conditions. The experiments were performed in a micro reactor using different metal catalysts. These catalysts were Raney-copper, Raney- nickel, Raney-cobalt, alumina-supported ruthenium and carbon-supported ruthenium. The temperature
range was 340-380°C and the pressure was between 150- 250 bar. Raney-nickel catalyst was found to be more active for glucose decomposition. Moreover, increasing the retention time up to 30 minute affected the gas yield. Madenoglu et.al. (2012) studied the catalytic hydrothermal gasification process on wheat straw as a biomass using a batch reactor at the subcritical water condition. The experiments were carried out over temperature range of 250- 300°C by using various catalysts which were alumina supported Pt, carbon supported Pt and Raney- Ni. The data highlighted that Raney- Ni is more active for the removal of the total organic carbon (TOC) from wheat straw and increased the gas yield efficiency.

Another study by Madenoglu et al. (2012) examined the hydrothermal gasification method on two types of agricultural residues, cotton and tobacco stalks, at a temperature range of 300-600 °C. The experiments were done under subcritical condition to study the effect of three different catalysts (Dolomite (CaMg (CO₃)₂), Trona (Na₃(CO₃)(HCO₃). 2H₂O), and Borax (Na₂B₄O₇. 10H₂O)). The main gas products in this study were carbon monoxide, carbon dioxide, hydrogen and methane whereas the main liquids were aldehydes, carboxylic acids, furfural and phenols. Trona gave the highest hydrogen yield compared with the other catalysts at 600°C.

Yao et al. (2012) studied the effect of the hydrothermal process on cellulose decomposition to reduce NiO to Ni at a low temperature of 250°C in an alkali medium by using NaOH. The results showed that cellulose was converted to acetic and lactic acids. On the other hand, NiO was found to be reduced without using any toxic or costly additive. Yin et al. (2012) investigated the conversion of cellulose to gasoline hydrocarbons in a batch reactor. These researchers observed that part of the cellulose was
converted to hydrogen by the steam reforming process and the second part was converted to 5- (hydroxymethyl) furfural (HMF) in the liquid phase at 300°C. The produced hydrogen reacted with HMF to form the main products, gasoline, which is composed of liquid alkanes. This study was done in the presence of a metal catalyst, Pt/Al₂O₃. The results indicated that this process of SR (H₂)-APD/H gave a higher yield of liquid alkanes compared with pyrolysis and hydrothermal liquefaction processes by 700 and 35 times, respectively. Although furfural was a product in the foregoing studies, no work has been performed on the catalytic sub/supercritical hydrothermal gasification of flax straw with the objective of optimizing furfural production.

2.3 THE PROPERTIES OF WATER AT SUBCRITICAL AND SUPERCRITICAL CONDITIONS

The properties of water change with the operating temperatures and pressures during the hydrothermal gasification process. There are two conditions that can be applied in the hydrothermal gasification of biomass. These depend on the condition of water. These are subcritical and supercritical. When the operating temperature and pressure are below the critical condition of water (374 °C and (21.8 MPa, 218 bar)) the process is deemed to be operated at subcritical conditions whereas at conditions higher than the critical condition, the process is considered as a supercritical process. At ambient temperature, water is considered to be a good solvent for ionic components and is not able to solve non-ionic chemicals. However, at supercritical conditions, water becomes a strong solvent even for non-ionic species. At subcritical water conditions, the number of ionic products of water is more than that at ambient temperature. Fig.2.1 shows the phase diagram of water at sub and supercritical conditions at different pressures and
temperatures (Kumar, 2010). Water at subcritical conditions becomes a suitable reactant medium for chemical reactions that involve ionic intermediate steps (Kruse, 2008). Furthermore, the dipole moment and pH of water decreases with increasing temperature (Brunner, 2009). The high critical point of water on its own is due to the strong hydrogen bonds between its molecules. The high dielectric constant of water at ambient temperature makes it not able to solve any organic compounds. As the temperature increases, the hydrogen bonds become weaker and the dissociation of water increases to form more ions (Kalinichev and Churakov, 1999). The nature of water changes to become more acidic at higher temperatures, which lead to the production of more hydronium ions for catalyzing acid reactions (Brunner, 2009).

According to Marcus (1999), when the temperature of water increases, its properties such as dielectric constant, viscosity and density decrease. The polarity of water reduces dramatically at the critical and supercritical regions. Also, the solubility of inorganic compounds in water decreases at the critical and supercritical regions while; on the other hand water becomes a suitable solvent for organic components. Moreover, water becomes more reactive at critical and supercritical regions than water at ambient temperature (Brunner, 2009). The low density of water at supercritical water conditions increases free-radical reactions, which in turn, increases the gasification efficiency (Kruse and Gawlik, 2003).
**Figure 2.1**: Phase diagram of water at sub- supercritical condition (Kumar, 2010).
2.4 HYDROTHERMAL GASIFICATION REACTION PATHWAYS

Sinag et al. (2003) has suggested reaction pathways for the hydrothermal gasification of biomass. These are shown in Figure 2.2. Sinag et al. (2003) indicated that the density of the phase is the key factor for changing the reaction from an ionic pathway to a free radical pathway and vice versa. Ionic reactions require a high phase density whereas free radical reactions taken place in a low phase density medium. The figure shows that cellulose decomposes to form glucose, which leads to the formation of furfural through the ionic pathway. On the other hand, the free radical reactions form acids, aldehydes and gases (Sinag et al., 2003).

2.5 THE PRODUCTION OF FURFURAL

Furfural is an aldehyde as well as an organic solvent with the formula of C₅H₄O₂. It is used to produce alkanes (Huber et al., 2006), and furan through catalytic decarboxylation reactions of furfural (Chheda and Dumesic, 2007). It is also used as an additive to produce lubricating oil. Furfural is also used with the condensation of acetone, formaldehyde, urea and phenol to make resins (Mckillip, 1981). Furfural can also be used as an intermediate for the production of fuels, pharmaceuticals and polymers (Runge and Zhang, 2012). Furfural can be produced from flax straw through ionic reactions (Harry, 2012). The production of furfural from flax straw occurs by the dehydration of pentoses or hexoses (Huber et al., 2006). Pentoses are found in the hemicellulose of lignocellulosic biomass. The dehydration of pentose to form furfural is shown in equations 2.1 and 2.2.
Figure 2.2: Reaction pathways in the hydrothermal gasification process (Dolan, 2010)
nC₅H₈O₄ (pentosan) + nH₂O (water) → nC₅H₁₀O₅ (pentose) \hspace{1cm} (2.1)

C₅H₁₀O₅ (pentose) - 3H₂O (water) → C₃H₄O₂ (furfural) \hspace{1cm} (2.2)

In the first reaction, pentosan is hydrated to form pentose followed by the dehydration of pentose to form furfural (Runge and Zhang, 2012). The production of furfural has been investigated by many researchers. Eken-Saracoglu et al. (1998) studied the kinetic degradation of two types of biomass, namely, seed hull of sunflower and corn cob through the hydrothermal technique to produce furfural in a batch reactor at the temperature range of 98 to 130 °C using sulfuric acid in the concentration range of 0.2 to 1 N as a catalyst to investigate the effect of reaction time on furfural production. Similarly, Mansilla et al. (1998) studied the production of furfural from rice hull using an autoclave reactor. Sulfuric acid, also used as catalysts, was added to the feed at different concentrations in the range of 3-35 wt%. The results showed that the highest yield of furfural was found by using 20 wt % of the acid catalyst. In addition, Garrote et al. (2001) made a similar study to investigate the kinetics of the degradation of corncobs to form furfural at temperatures between 145 to 190 °C using a hydrothermal process in a stainless steel batch reactor. The study showed that the kinetics of degradation was dependent on the operating temperature.

Several research groups (Aguilar et al., 2002; Lavarack et al., 2002; Tellez-Luis et al., 2002) have developed a kinetic model for the producing furfural and other products by the hydrolysis of sugar cane bagasse and sorghum straw with the addition of sulfuric acid or hydrochloric acid. These experiments were carried out using H₂SO₄ and HCl in the concentration range of 0.25-8wt % at a temperature range of 80 to 200 °C. Aguilar et al. (2002) observed that about 90% of sugar cane bagasse was hydrolysed after 24 min of
reaction time at 122 °C using 2% H₂SO₄. On the other hand, Lavarack et al. (2002) concluded that by using sulfuric acid, the hydrolysis of sugar cane bagasse increased compared with HCl acid. Tellez-Luis et al. (2002) also indicated that the optimum yield of furfural was obtained at 122 °C with 2% H₂SO₄ but after 71 min of reaction time. In terms of acid catalysis, Montane et al. (2002) have explained the effect of adding sulfuric acid at the concentration range of 0.05- 0.250 mol/L on the hydrolysis of olive stones in a continuous tubular reactor at the operational temperature range of 220- 240 °C with a short residence time of few minutes. The maximum furfural yield was in a range of 50 to 65 wt%. The operational temperature and the concentration of the acid catalyst played important roles on furfural production. However, the highest furfural yield was found at 150 s 240 °C using 0.250 mol/L of sulfuric acid. Moreover, Herrerat et al. (2003; 2004) used sorghum straw as the feedstock to obtain an optimum yield of furfural at 122 °C, 70 min of reaction time, and 6 % of HCl. Furthermore, these researchers observed that a residence time of 83 min was the most suitable to get the optimum yield of furfural of 0.8 g/L at 100 °C.

Karimi et al. (2006) studied the hydrolysis of rice straw to produce furfural using H₂SO₄ in the concentration range of 0- 1%. The experiments were carried out at pressures ranging from 10 to 35 bars. The furfural yield found to be dependant on the operational pressure. In separate work, Rahman et al. (2006) studied the hydrolysis of oil palm empty fruit bunch using H₂SO₄ at concentrations in the range of 2-6 % for producing furfural at 120 °C. The reaction time ranged between 0 -90 min. The results showed that the highest yield of furfural was obtained at 6% of H₂SO₄ at 120 °C and 15 min of reaction time. Meanwhile, Vazquez et al. (2007) performed the hydrolysis of sorghum straw to produce
furfural using phosphoric acid at a concentration of between 2-6 % with reaction time ranging from 0 to 300 min at the temperature of 134 °C. The optimum conditions for producing furfural were 134 °C, 300 min of reaction time and 6% of H₃PO₄. Recently, Yat et al. (2008) investigated the hydrothermal gasification of different feeds such as timber of aspen, basswood, red maple, balsam fir and switchgrass using a batch reactor at a temperature range of 160 to 190 °C. The catalyst used in this study was H₂SO₄ in the concentration range of 0.25 to 1.0 w/v%. The results showed that furfural production was found to be sensitive to the acid concentration and the operating temperature of the process. More recently, Lenihan et al. (2010) studied the hydrolysis of potato peel for producing furfural at 135 to 200 °C in a batch reactor using a phosphoric acid catalyst at concentrations ranging from 2.5 to 10% w/w. The results indicated that the optimum conditions for producing furfural were 8 min reaction time, 10 % w/w acid concentration, and 135 °C. Currently, Bamufleh et al. (2013) have investigated the hydrolysis of the midribs of the sukkaria tree (date – palm) for producing furfural using different concentrations of sulfuric acid as catalysts. The concentrations of the acid ranged from 5 to 15wt% at temperatures in the range of 100- 140 °C. The highest yield of furfural was obtained at 140 °C using 15wt % of H₂SO₄. In all these cases of producing furfural from different cellulosic biomass, homogeneous acid catalysis was employed. Even though furfural could be obtained as a product, its separation from the liquid catalyst could pose a challenge. This would necessitate the use of solid acid catalysts.
2.6 THE PROPERTIES OF SOLID ACID CATALYSTS

There are many types of solid acid catalysts. Three common types are H-ZSM-5, silica-alumina and γ-alumina. H-ZSM-5 is a zeolite type catalyst with a crystalline porous structure and contains SiO\textsubscript{4} and AlO\textsubscript{4}. ZSM-5 is one of the zeolites types, which consists of 5-silica-alumina molecules arranged in the form of a pentagon. The pentagons are linked with oxygen atoms (Bhatia, 1989). According to Olson et al. (1981), the content of Al in ZSM-5 affects the properties of the catalyst such as catalytic activity, water content and ion exchange capacity. Also, the ratio of the Si to Al affects the ZSM-5 hydrophobic nature (Chen, 1976). Altering ZSM-5 through ion exchange of different cations such as Na\textsuperscript{+} with H\textsuperscript{+} will form H-ZSM-5, which increases the catalyst selectivity and activity. H-ZSM-5 is found to have more acidity compared with ZSM-5 because of the existence of more protons H-ZSM-5 than ZSM-5 (Furrer, 1988). H-ZSM-5 is found to have more ability to convert different feed types such as methanol and alcohols to form hydrocarbons (Derouane et al., 1978).

Silica-alumina catalyst is one of the amorphous solid acid catalysts, which contains Lewis and Brønsted acid sites. Silica-alumina consists of silicon and aluminum atoms. The silicon atom is bonded with four atoms of oxygen and the aluminum is bonded with three atoms of oxygen (Katikaneni et al., 1995). Silica-alumina is used mainly in the cracking reactions of cumene and heptane as well as m-xylene isomerization (Sato et al., 2001). The third solid acid catalyst example is γ-alumina, which is one of the microporous solid acid catalysts (Pinto et al., 2004). It has a crystalline structure (Wolverton and Hass, 2000; Gutierrez et al., 2001). It is used in the
petrochemical and refinery processes. It is widely used in the clauss process and for the dehydration of alcohols (Digne et al., 2004).

2.7 HYDROTHERMAL GASIFICATION OF BIOMASS USING SOLID ACID CATALYSTS

Researchers have suggested that using solid acid catalysts for extracting useful chemicals out of biomass gives high selectivity, and high ability for converting the lignocellulosic material to form biofuels. The solid acid catalysts can be used instead of liquid acid catalysts because they can be separated from the products more easily than the liquid catalysts. Besides, the solid acid catalysts can be recycled to give long time of activity (Guo et al., 2012).

Onda, et al. (2008) studied hydrothermal gasification using cellulose to produce glucose. The catalysts used in this study were sulfated, sulfonated, and H form of zeolite. The results showed a high glucose yield of 90%. The sulfonated activated – carbon gave the highest yield of glucose compared to the other two catalysts. Hara (2010) investigated the effect of carbon-based solid acid catalyst, which has sulfonic acid groups. The study was focused on using cellulose through a hydrolysis process to produce biodiesel. The results showed that using this type of catalyst increased the conversion efficiency of the biomass. Hegner, et al. (2010) studied the hydrolysis of cellulose to produce glucose and levulinic acid using solid-supported acid catalysts Nafion (SAC 13) and FeCl$_3$/silica in a flow reactor at 190 °C. The data showed that these catalysts had high activity to produce biofuel. Nafion (SAC 13) gave the highest conversion of cellulose.

Yang et al. (2011) discussed the effect of using solid acid catalyst, niobic catalyst treated with phosphoric acid (NA-P), on the hydrolysis of different biomass types. Model
compounds were used in the investigation of monosaccharide, polysaccharide and Jerusalem artichoke juice to produce 5- hydromethylfurfural (5-HMF). The experiments were carried out using a batch reactor at 433 K. The results showed that using NA-P increased the biomass conversion with high yields of 5-HMF for inulin, fructose, glucose and Jerusalem artichoke juice of 54, 89, 49 and 65% respectively.

Recently, Ormsby et al. (2012) studied the hydrolysis of hemicellulose by using solid acid carbon catalyst (biochar) and activated carbon (AC). The experiments were carried out at temperatures in the range of 90 - 120 °C using a batch reactor. The results showed that activated carbon has a higher surface area compared with biochar. However, higher xylan conversion was obtained from biochar with higher hydrolysis reaction rate compared with (AC). The conversion of xylan reached 85% at 120 °C and 2 hr reaction by using biochar and 57% conversion at 24 hr and 120 °C by using (AC). In addition, the rate of reaction and the conversion were found to increase with an increase in temperature. More recently, a study was performed by Zhang et al. (2013) to investigate the hydrothermal gasification of rice straw using solid acid catalysts. The reaction was carried out in two steps. First, the rice straw was hydrolyzed to form glucose, and then hydrogenated to sugar alcohol (sorbitol and mannitol) using hydrogen that came from ethanol steam reforming. The experiments were performed in a batch reactor. The investigation showed that using Pt/γ-alumina at 503 K increased the rice straw conversion to 73.1 % with a mannitol yield of 5.5% and a sorbitol of 0.8%. On the other hand, the addition of H-ZSM-5 to the catalyst increased the yield of mannitol and sorbitol up to 6.8% and 8.5%, respectively at 463 K. There has been no report so far on studies on the catalytic subcritical hydrothermal gasification of flax straw to produce furfural. It is
therefore essential to determine how solid acid catalysts will influence the yield of furfural from flax straw.
CHAPTER 3
EXPERIMENTAL PROCEDURE

3.1 SUMMARY OF THE EXPERIMENTAL PROCEDURE

This study covered a total of 60 experimental runs to evaluate the effects of different experimental parameters (temperature, residence time, initial gauge pressure, and weight of solid acid catalysts) on the production of furfural and phenol by the subcritical hydrothermal gasification of flax straw. These experiments were carried out using an autoclave batch reactor. The experimental setup and typical experimental procedures are described in the following sections of this chapter. Furthermore, preparation of the feed and analysis of the products are also described in this chapter.

3.2 CHEMICALS, GASES AND EQUIPMENT

The following chemicals, gases and equipment were used for this research.

3.2.1 Chemicals

- Ethylene glycol bath fluid (Cole-Parmer)

3.2.2 Gases

- Nitrogen (UHP, Praxair)
- Helium (UHP, Praxair)

3.2.3 Equipments

- 600 ml Stainless steel batch reactor (Model 5523, Parr Instrument Co., obtained from Illinois, USA)
- Temperature Controller (Model 4836, Parr Instrument Co., obtained from Illinois, USA)
• GC-MS (Model 6890/5073, Hewlett-Packard Canada Ltd., Canada)
• Auto injector (Model 7683, Hewlett-Packard Canada Ltd., Canada)
• GC/TCD (Agilent 6890 N, USA)
• Flax Straw Chopper

3.3 FEED MATERIALS AND PREPARATION

Flax straw (Linum Usitatissimum) was obtained from farms located in rural areas in Regina, Saskatchewan, Canada. A flax straw chopper was used to chop the flax straw to a size of 1-3 mm. Table 3.1 shows the elemental composition (i.e. of carbon, hydrogen, nitrogen, oxygen, sulphur) and moisture in flax straw.

Table 3.1: Elemental analysis of flax straw

<table>
<thead>
<tr>
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</thead>
<tbody>
<tr>
<td>Carbon (wt%)</td>
<td>48.10</td>
<td>45.24</td>
<td>49.1</td>
</tr>
<tr>
<td>Hydrogen (wt%)</td>
<td>5.78</td>
<td>6.25</td>
<td>6.1</td>
</tr>
<tr>
<td>Nitrogen (wt%)</td>
<td>0.68</td>
<td>1.01</td>
<td>1.3</td>
</tr>
<tr>
<td>Ash (wt%)</td>
<td>4.18</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Sulphur (wt%)</td>
<td>0.07</td>
<td>1.18</td>
<td>0.12</td>
</tr>
<tr>
<td>Oxygen (wt%)</td>
<td>41.91</td>
<td>43.29</td>
<td>40.5</td>
</tr>
</tbody>
</table>
Three types of solid acid catalysts were used in this study, namely, H-ZSM-5, γ–alumina and silica-alumina. H-ZSM-5 was purchased from ZEOCHEM AG, Switzerland. The trade name of H-ZSM-5 is ZEOcat which is a zeolite type of catalyst with a high acidity and high silica to alumina ratio in the range of 20-30 as shown in Table 3.2. The γ–alumina was purchased from EM science, Merck KGa A, Darmstadt Germany. Silica-alumina was obtained from Sigma Aldrich with silica to alumina ratio of 10 mol/mol. The amount of each of the three catalysts used in this study was in the range of 0.5-1.5 g weighed by a chemical balance (PB602-S, Mettler Toledo, Switzerland). The ratio of silica to alumina of H-ZSM-5, silica–alumina and γ-alumina is shown in Table 3.2.

**Table 3.2:** The ratio of silica to alumina in silica-alumina, H-ZSM-5 and γ–alumina

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>SiO$_2$/Al$_2$O$_3$ (mol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-ZSM-5</td>
<td>20-30</td>
</tr>
<tr>
<td>silica-alumina</td>
<td>10</td>
</tr>
<tr>
<td>γ–alumina</td>
<td>0</td>
</tr>
</tbody>
</table>
3.5 REACTION FEED STOCK

The feed of this project was flax straw pieces in suspension in water. The weight of flax straw (WA0) used in all the experiments was 10 g corresponding to 10 wt% with 90 g water corresponding to 90 wt%. The weight of 10 g flax straw was based on a previous study on the non-catalytic hydrothermal gasification of flax straw (Harry, 2012).

3.6 OPERATING CONDITIONS

The experiments were performed to study the effects of different operating conditions (temperature, initial gauge pressure, retention time and the weight of solid acid catalyst) on the yield of furfural and phenol as well as the gas yield for the subcritical hydrothermal gasification of flax straw. The retention time is considered as the isothermal time duration of the process after it has reached the desired temperature. After the desired retention time is reached at the desired temperature, the process is cooled. The experiments were categorized into two groups based on the initial gauge pressure. These were: autogenous pressure experiments and non-autogenous pressure experiments. In the autogenous pressure experiments, the initial gauge pressure was set at atmospheric pressure while the other experimental parameters were varied. On the other hand, in the non-autogenous pressure experiments, an external pressure was provided from a nitrogen cylinder before starting the reaction. In this group of experiments the initial gauge pressure was the varied factor whereas other experimental conditions were kept constant. The objective of performing the non-autogenous pressure experiments was to study the effect of pressure on the yield of furfural while using the optimum conditions obtained from other experimental parameters, as determined previously from the autogenous pressure experiments. The amounts of the three solid acid catalysts (H-ZSM-5, γ-
alumina, and silica-alumina) were varied in order to obtain the optimum weight of catalyst for the production of fufural. The ranges of the experimental parameters used in this study were as follows:

- Temperature: 200, 225, 250, 275, 300 and 325 °C
- Pressure (initial gauge pressure): 0, 20, 40 and 60 bar
- Retention time: 0, 60, 90 and 120 min
- Concentration of flax straw: 10 wt%
- Solid acid catalyst amount: 0.5, 1.0 and 1.5 g.

3.7 EXPERIMENTAL SETUP AND PROCEDURE

3.7.1 Schematic Diagram and Description of Experimental Setup

Figure 3.1 shows the schematic diagram of the experimental setup that was used in this study. The experiments were performed in 600 mL stainless steel batch reactor (model 5523, Parr Instrument Co., Moline, IL). The reactor has a removable head, which consists of a magnetic drive attached to a stainless steel (T316) stirring shaft. The stirring shaft has two impellers (diameter 1.5 inch) of four rectangular blades. The first impeller is positioned in the bottom of the reactor whereas the second impeller is located 2.5 inches above the bottom impeller. Furthermore, the reactor head has a Bourdon-type pressure gauge with a measuring capacity of 0 – 3000 psi (0 – 200 bar). The reactor head has three valves for gas inlet, gas release and liquid sampling with a preset safety rupture disk that explodes in the case of over-pressurizing. Moreover, the reactor has a J-type thermocouple for measuring the temperature of the reaction mixture while using a cooling coil for maintaining the temperature at constant value throughout the process.
The reactor also has a dip tube used for gas introduction and sample removal. A solenoid valve is used in the cooling system for regulation purposes. The reactor has a temperature controller (model 4836, Parr Instrument Co., Moline, IL) for regulating the reactor furnace to supply the desired amount of heat to the reactor. The accuracy of the temperature controller is within (± 0.1%). Ultra-high-purity (UHP) nitrogen cylinder was used for purging the system, and this was provided by Praxair (Ontario, Canada).

CHNO analysis for the flax straw and the char samples

**Figure 3.1**: Schematic diagram of the experimental setup in this study (Harry, 2012)
3.7.2 Typical Experimental Run

The weight of flax straw \((W_{A_0})\) used in this study was 10 g, which was weighed using a chemical balance. The weight of water was 90 g, which added to the flax straw to achieve the concentration of 10 wt% flax straw in suspension. The concentration of the flax straw was constant at 10 wt% in all the experimental runs. The specific weight of the solid acid catalyst was weighed and added to the mixture. Three solid acid catalysts used were H-ZSM-5, \(\gamma\)-alumina and silica-alumina each of weights of 0.5, 1, and 1.5 g of particle size of 1.18 mm. After the entire mixture was placed in the autoclave batch reactor, the reactor was purged using nitrogen gas for 10 min to remove air from the reactor before starting the reaction. The reactor was then heated until it reached the desired operating temperature (i.e. 200, 225, 250, 275, 300 or 325 °C) and was maintained at that temperature for a specific residence time (0, 60, 90 and 120 min). At the completion the residence time of the reaction, the reactor was cooled to the room temperature. The gas product was analyzed by an online gas chromatograph (GC) which was equipped with a thermal conductivity detector (GC-TCD) and the compositions of the gases are recorded. After cooling, the liquid product was filtered to separate it from char that was formed in some cases during the reaction. The filtered liquid sample was analyzed by GC-MS for quantifying the target liquid products. Moreover, the char samples were analyzed using elemental analysis (CHNS) procedure to determine the elemental content of carbon, hydrogen, nitrogen and sulphur. In the non-autogenous experiments, a nitrogen gas cylinder was used to supply the specific initial gauge pressure (20, 40, and 60 bar) before starting the experiment.
3.8 SAFETY PRECAUTIONS

Safety precautions were considered before and during each experimental run. These are listed below:

- Wearing safety eye glasses and lab jacket.
- Closing the reactor and performing a leak test by applying nitrogen pressure inside the reactor and observing the pressure drop with the time.
- Checking that the nitrogen cylinder is firmly closed.
- Ensuring that the plastic tubes of the cooling system do not touch any hot metallic parts during the reaction to avoid the melting and leaking of the cooling liquid (Ethylene Glycol).

3.9 PRODUCT ANALYSIS

3.9.1 Gaseous Product Analysis

The gas product was analyzed using a gas chromatograph (Agilent Technologies 6890) equipped with two columns (Hayesep Q and molecular sieve) and a thermal conductivity detector (TCD). The calibration of GC was performed using standard gas mixtures (H₂, CO, CO₂, CH₄, C₂H₆O₂, and N₂) to obtain the compositions of the gases in the gas product. Helium gas was used as the carrier gas in the GC analysis.
3.9.2 Liquid Products Analysis

The concentrations of furfural and phenol were obtained using a gas chromatograph attached to a mass selective detector (GC-MS). Gas chromatograph (GC) was used to separate the chemicals of the liquid sample while the obtained mass spectra (MS) were used for identification of the chemicals. The combination of GC and MS provided the separation and identification of the liquid chemicals in one injection. The GC-MS used in this study (model 6890/5073) was obtained from Hewlett-Packard Canada Ltd., Montreal, Quebec, Canada. HP-35 MS chromatographic capillary column having cross-linked poly(ethylene glycol) of intermediate polarity was used based on a previous study of non-catalytic hydrothermal gasification of flax straw (Harry, 2012). The dimensions of the column were: 0.25 µm thickness x 0.25 mm i.d x 30 cm length, and this was obtained from Hewlett-Packard Canada, Ltd., Montreal, Quebec, Canada. The liquid sample was filtered by 0.2 µm nylon membrane before injecting in the GC-MS. The liquid sample of volume 1 µL was injected into the GC using an auto sampler/auto injector (model 7683, Hewlett-Packard Canada Ltd., Montreal, Quebec, Canada). The reproducibility of the auto injector volume was within 0.3% relative standard deviation (RSD) of the percentage of peak areas. The inlet temperature was 250 °C while the split ratio was 5:1. The initial oven temperature was set at 37 °C and ramped to 210 °C at a rate of 10 °C/min. The final temperature was kept for 20 min to ensure that all of the liquid chemicals were separated and eluted completely. Helium gas of ultra-high purity (UHP) was used as the carrier gas at a flow rate of 1mL/min. The temperatures used for GC-MS interface, MS quadrupole and MS source were 250, 150 and 230 °C, respectively. A mass range of 10 – 300 was used in MS scan mode with EM
voltage of 1858 V. The commercial database of the National Institute of Standards and Technology (NIST, 1998 version) was used to identify liquid components by matching the peaks mass spectra of the components with the mass spectra in the database. The target products were verified by matching the peak mass spectra and the GC retention time of commercial pure standards of the products with the peak mass spectra and GC retention time of the target products in the experimental liquid samples. The peak mass spectra of the commercial pure standards and the products in the experimental liquid samples were compared using NIST database. A percentage matching of 95% was accepted as a good match.

3.10 CATALYST CHARACTERIZATION

3.10.1 X-ray Diffraction Measurements

Powder X-ray diffraction (XRD) was performed for characterizing the degree of crystallinity of fresh solid acid catalysts. A dried catalyst was used to perform the test using Bruker model D8/GADD diffractometer using Cu Kα radiation (λ = 1.5418 A°). The electric current was 40 mA with a voltage of 40 KV. The scanning rate was 5°/min with a 2θ scanning range of 20° – 80°. The run was carried out using a powder sample that was placed in a sample holder and scanned to get the range of 2θ, which reflected the crystallinity phases.

3.10.2 Specific Surface Area and Pore Size Distribution Analysis

Surface area and pore size distribution of the three solid acid catalyst used in this study (H-ZSM-5, γ–alumina and silica-alumina) were measured using N₂ physisorption. N₂ physisorption was performed using Micromeritics ASAP 2010 apparatus at liquid
nitrogen temperature. The catalyst sample was degassed for four hours at 180 °C under vacuum before starting the analysis. The average pore volume and pore size distribution were measured by the desorption branch of the N2-isotherm.

3.10.3 Temperature Programmed Oxidation (TPO)

Temperature Programmed Oxidation of the catalyst was used to investigate any carbon deposited on catalysts during the hydrothermal gasification process. TPO analysis was performed using Shimadzu TGA/Fc-60A instrument, which contained an ultra-sensitive weighing device. TPO analysis was performed by heating the used catalyst from ambient temperature to 800 °C at a heating rate of 15 °C/min using 5% O2/bal.N2 at a flow rate of 20 ml/min.

3.11 EQUATIONS USED TO CALCULATE YIELD AND CONVERSION

The general equation that describes the catalytic hydrothermal gasification of flax straw in subcritical water is written below:

\[
\text{CH}_{1.5}\text{O}_{0.62} + \text{H}_2\text{O} \xrightarrow{\text{ACID CATALYST}} \text{CO} + \text{CO}_2 + \text{CH}_4 + \text{char} + \text{liquid products} + \text{tar (CH}_n\text{O}_x) + \text{H}_2\text{O}
\]  

(3.1)

This equation was used in the kinetic study of the catalytic hydrothermal gasification of flax straw in subcritical water. The yield of gas was calculated as the mole of the component divided by the grams of flax straw used as feed for the process. The yield of the gas products can be calculated as follows:

\[
\text{Yield of “A”} = \frac{\text{mol of “A”}}{\text{gram of flax straw used}} \left( \frac{\text{mol}}{\text{g}} \right)
\]  

(3.2)
On the other hand the yield of liquid products was calculated as the weight (g) of liquid per weight (g) of flax straw used in the experiment. The yield of the liquid can be described as

\[
\text{Yield of "A"} = \frac{\text{gram of "A"}}{\text{gram of flax straw used}} \quad (\frac{g}{g})
\]

(3.3)

Where “A” is the gas or liquid product

The carbon conversion of the flax straw can be calculated as the difference between the carbon content in original flax straw and the carbon content in the char samples collected at the end of the reaction divided by the carbon content in the original flax straw. The carbon conversion is calculated by the following equation:

\[
X_c = \frac{W_{ci} - W_c}{W_{ci}}
\]

(3.4)

where:

\( W_{ci} \) = initial weight of carbon in the original flax straw before the reaction.

\( W_c \) = weight of carbon in the char at the end of the reaction.
CHAPTER 4

RESULTS AND DISCUSSION

4.1 CATALYSTS CHARACTERIZATION

4.1.1 BET Surface Area and Pore Size Distribution

BET surface area and pore size distribution of the solid acid catalysts (H-ZSM-5, γ-alumina and silica-alumina) were measured by N₂ physisorption. The results of BET surface area and pore size distribution are shown in table 4.1. The BET surface area of γ-alumina and H-ZSM-5 were comparable whereas silica-alumina showed the highest BET surface area. Silica-alumina and γ-alumina displayed comparable pore size values while H-ZSM-5 gave the lowest pore size value. Silica-alumina and γ-alumina were in mesoporous range of 20 – 500 Å which was in good agreement with previous studies (Bhatia, 1989; Satterfield, 1991; Katikaneni et al., 1998; Pathak, 2005). The highest pore volume was exhibited by silica-alumina whilst the lowest pore volume was obtained for H-ZSM-5.
Table 4.1: BET surface area, pore size, and pore volume of different solid acid catalysts used in this study

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>BET surface area m²/g</th>
<th>Average pore size Å</th>
<th>Pore volume cm³/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-ZSM-5 (Pathak, 2005)</td>
<td>319</td>
<td>5.4</td>
<td>0.16</td>
</tr>
<tr>
<td>γ–alumina</td>
<td>291.95</td>
<td>34.7</td>
<td>0.225</td>
</tr>
<tr>
<td>silica-alumina</td>
<td>482</td>
<td>45.4</td>
<td>0.698</td>
</tr>
</tbody>
</table>

4.1.2 X-ray Diffraction (XRD)

X-ray diffraction was performed to investigate the crystalline structure of the solid acid catalysts used in this study. X-ray diffractions of H-ZSM-5, γ–alumina and silica-alumina are shown in figures 4.1, 4.2. Crystalline structures were obtained for γ–alumina and H-ZSM-5 whereas there was no crystalline structure for silica-alumina. These observations are in a good agreement with previous studies (Szostak, 1992; Zhong et al., 2001; Rinaldi and Schuchardt, 2004; Pathak, 2005).
Figure 4.1: X-ray diffraction of γ–alumina and silica-alumina (this study)

Figure 4.2: X-ray diffraction of different solid acid catalysts (Pathak, 2005)
4.1.3 Fourier Transformed Infrared Spectroscopy (FTIR)

According to Pathak (2005), FTIR can be performed using pyridine to investigate Brønsted and Lewis acid sites on solid acid catalysts. Figure 4.3 shows the FTIR spectra for the three catalysts (H-ZSM-5, γ–alumina, and silica-alumina). The acid sites are labelled as (B) for Brønsted and (L) for Lewis acid sites. Gamma-alumina had mainly Lewis acidity while silica-alumina had Brønsted acidity obtained at 1650 cm\(^{-1}\) and 1560 cm\(^{-1}\), respectively. These results are confirmed by previous studies (Plyuto et al., 1999; Dabbagh et al., 2005). H-ZSM-5 showed the two types of acidity as Brønsted at 1560 cm\(^{-1}\) and Lewis at (1510 cm\(^{-1}\), 1660 cm\(^{-1}\)). These results of H-ZSM-5 are in a good agreement with those of Adjaye et al. (1996) and Anand et al. (2003).
Figure 4.3: FTIR spectra of different solid acid catalysts using pyridine (Pathak, 2005)
4.1.4 Temperature Programmed Desorption (TPD)

The temperature programmed desorption was measured by Pathak (2005) using ammonia to investigate the strength of acidity in the solid acid catalysts. The temperature programmed desorption data for H-ZSM-5, γ-alumina and silica-alumina are shown in Figure 4.4. The measurement was focused on the desorption temperature which reflects the strength of acidity of the acid sites. A high desorption temperature corresponds to a high acid strength and vice versa. According to Lewandowski and Sarbak (2000), the temperature of desorption of ammonia is classified into three ranges, namely, weak acid centers (20 – 200 °C), intermediate acid centers (200 – 350 °C) and strong acid centers (350 – 550 °C). The number of acid sites is related to desorption peak intensity. Two peaks appeared in the TPD spectrum of H-ZSM-5 at 250 and after 400 °C, which correspond to intermediate acid sites and strong acid sites, respectively. The intensity of the first peak at 250 °C is higher than the intensity of the second peak. This implies that the number of intermediate acid sites is more than the number of strong acid sites. These results are in good agreement with previous studies (Anderson et al., 1979; katikaneni et al., 1998). The TPD curve of γ–alumina showed weak acid centers at 130 °C and strong acid centers at 620 °C. The TPD curve of silica-alumina displayed weak acid centers at temperatures less than 200 °C. The highest desorption temperature of ammonia was exhibited by γ-alumina at 620 °C. This implies that γ–alumina has the highest acidity strength compared with H-ZSM-5 and silica-alumina.
**Figure 4.4**: Temperature programmed desorption (TPD) for different solid acid catalysts (Pathak, 2005)
4.1.5 Temperature Programmed Oxidation (TPO)

Temperature programmed oxidation was performed on the catalysts (γ-alumina, H-ZSM-5, silica-alumina) to investigate any carbon deposition on the catalysts after performing the experiments. The TPO analysis was performed using samples of the three catalysts at the optimum temperature (250 °C) of producing furfural by γ-alumina of the highest performance in this study compared with the other two catalysts. The TPO curves of γ-alumina, H-ZSM-5 and silica-alumina are shown in Figures 4.5, 4.6 and 4.7, respectively. All the three figures show that the char and carbon were burned at ranges of 200 – 400 °C and 400 – 600 °C, respectively. The carbon deposition on the catalysts decreased following the trend: γ-alumina > H-ZSM-5> silica-alumina. Table 4.2 shows the carbon deposition on the three solid acid catalysts. The highest carbon deposition was found on γ-alumina which has a kind of high pore size and that could lead to more carbon deposition on the surface of the catalyst.

Table 4.2: Temperature programmed oxidation analysis of the three catalysts

<table>
<thead>
<tr>
<th>catalyst</th>
<th>Weight of catalyst (g)</th>
<th>Weight of carbon (g)</th>
<th>g C/ g cat./ min</th>
</tr>
</thead>
<tbody>
<tr>
<td>γ–alumina</td>
<td>0.00657</td>
<td>0.00231</td>
<td>0.352</td>
</tr>
<tr>
<td>H-ZSM-5</td>
<td>0.0188</td>
<td>0.00142</td>
<td>0.076</td>
</tr>
<tr>
<td>silica-alumina</td>
<td>0.0135</td>
<td>0.00089</td>
<td>0.066</td>
</tr>
</tbody>
</table>
Figure 4.5: Temperature Programmed Oxidation of γ–alumina at 250 °C
Figure 4.6: Temperature Programmed Oxidation of H-ZSM-5 at 250 °C.
Figure 4.7: Temperature Programmed Oxidation of silica-alumina at 250 °C
4.2 EFFECT OF EXPERIMENTAL PARAMETERS ON FUFURAL AND GAS YIELDS WITH SOLID ACID CATALYSTS

4.2.1. Effect of Temperature on Furfural and Gas Yields

The optimization of the operational temperature for the furfural production was carried out using six different temperatures (200, 225, 250, 275, 300 and 325 °C) using 10wt% of flax straw. The experiments were performed using three different types of solid catalysts (H-ZSM-5, silica-alumina, and γ–alumina). In each run 1g of catalyst was used for a retention time of 0 min and 0 bar as the initial gauge pressure of the reactor. Figure 4.8 shows the effect of temperature on the furfural yield using these three catalysts compared with the non-catalytic experiments for furfural yield at 250 and 325 °C. The results showed that the furfural yield decreases with increasing temperature up to 325 °C. On the other hand, the formation of phenol increases at higher temperatures (275-325°C), which shows good agreement with the non-catalytic study (Harry, 2012). The reduction in furfural yield at higher temperatures increases the yields of phenol and gases. The optimum temperature of producing furfural with H-ZSM-5 and γ–alumina was 250 °C, and 225 °C for silica-alumina. The highest yield of furfural at 250 °C was 0.005822 g/g using 1 g of γ-alumina per 10 g flax straw. The use of solid acid catalysts decreases the optimum temperature of furfural production from 275 °C for the non-catalytic study (Harry, 2012) to 250 °C with H-ZSM-5 or γ–alumina, and 225 °C with silica-alumina. The highest yield of furfural was obtained using γ–alumina compared with the other two catalysts. The presence of silica elements in the H-ZSM-5 and silica-alumina decreased the yield of furfural. Moreover, the effect of temperature on furfural, phenol and gas
yields using 1g of catalysts (H-ZSM-5, γ-alumina, and silica-alumina) is shown in Figures 4.8, 4.9 and 4.10, respectively. Higher operating temperatures favoured phenol and gas production.

![Figure 4.8: Effect of the temperature on the yield of furfural at retention reaction time 0 min, 10 wt % flax straw, 1g catalyst and 0 bar as initial gauge pressure of the reactor.](image)
Figure 4.9: Effect of the temperature on the yield of phenol at 1g catalyst, retention reaction time 0 min, 10 wt % flax straw, and 0 bar as initial gauge pressure of the reactor.

Figure 4.10: Effect of the temperature on the gas yield at 1g catalyst, retention reaction time 0 min, 10 wt % flax straw, and 0 bar as initial gauge pressure of the reactor.
4.2.2. Effect of Retention Time on Furfural and Gas Yields

The effect of retention time on furfural and gas yields was investigated at 0, 60 and 120 min as a comparison between the three solid acid catalysts at 250 °C for silica-alumina and γ–alumina, and at 225 °C for H-ZSM-5. The concentration of flax straw was 10 wt % and the initial gauge pressure was 0 bar. Figure 4.11 shows the effect of the retention time on the yield of furfural using 1g of catalyst (H-ZSM-5, γ–alumina, and silica-alumina). In this study, the same conclusion of decreasing furfural yield for increasing retention time was reached for the three catalysts. Furfural yield decreased because of increased gasification efficiency with increased retention time. This results in the formation of a larger amount of gas. This conclusion is in perfect agreement with the results obtained in the non-catalytic subcritical hydrothermal gasification of flax straw (Harry, 2012). Figure 4.12 explains the effect of the retention time on the gas yield using 1g catalyst (H-ZSM-5, γ–alumina and silica-alumina). The results showed that the gas yield was observed to increase as the reaction retention time increased for all of the three solid acid catalysts.
Figure 4.11: The effect of the retention time on the yield of furfural at 1g catalyst, 250 °C for silica-alumina and γ–alumina and 225 °C for H-ZSM-5, 10 wt % flax straw, and 0 bar as initial gauge pressure of the reactor.

Figure 4.12: The effect of the retention time on the gas yield at 1g catalyst, 250 °C for silica-alumina and γ–alumina and 225 °C for H-ZSM-5, 10 wt % flax straw, and 0 bar as initial gauge pressure of the reactor.
4.2.3. Effect of The Catalyst Weight/ Flax Straw Weight Ratio on Furfural and Gas Yields

The effect of the catalyst weight/flax straw weight ratio for H-ZSM-5, silica-alumina and γ–alumina was tested in the weight ratio range of 0.05 – 0.15 g to obtain the optimum catalyst weight/flax straw weight ratio (W/WA₀) for furfural production. The experiments were carried out at 250 °C, 0 min, autogeneous gauge pressure, and 10 g (i.e. 10 wt%) of flax straw. The effect of W/WA₀ on furfural yield is shown in Figure 4.13. Generally, furfural yield increased as the catalyst weight or W/WA₀ increased up to 1.0 g of catalyst or W/WA₀ of 0.1. Beyond this weight or W/WA₀, the yield of furfural decreased. The optimum W/WA₀ was 0.1 for all the three catalysts. The highest furfural yield was obtained with γ–alumina compared to the other two catalysts, H-ZSM-5 and silica-alumina. It is clear that the rate of gasification increased by increasing the weight of catalyst or W/WA₀ beyond 1 g, or 0.1, respectively resulting in the formation of a larger yield of gas while the furfural yield decreased. Figure 4.14 shows the direct effect of the catalyst weight or W/WA₀ on the gas yield. The figure shows that the total gas yield increases as the catalyst weight or W/WA₀ increases for all the three catalysts. A higher weight of catalyst or W/WA₀ is used to increase the gas yield at subcritical condition by increasing the rate of contribution of the free radical pathway to the overall reaction.
**Figure 4.13:** The effect of the catalyst weight on the yield of furfural at retention reaction time 0 min, 10 wt% flax straw, temperature of 250 °C, and 0 bar as initial gauge pressure of the reactor.

**Figure 4.14:** The effect of the catalyst weight on the gas yield at retention reaction time 0 min, 10 wt% flax straw, temperature of 250 °C and 0 bar as initial gauge pressure of the reactor.
4.2.4. The Effect of The Pressure on Furfural and Gas Yields

The effect of the initial gauge pressure on the furfural and gas yields was investigated using 1 g (or W/WA₀ of 0.1) of the solid acid catalysts (H-ZSM-5, silica-alumina, and γ–alumina). Different initial gauge pressures of 0, 20, 40 and 60 bar were applied on the reactor using high purity N₂ gas at a retention time of 0 min, and 10wt% flax straw. The study of the initial gauge pressure was carried out at three different temperatures (225, 250, and 275 °C). The effects of the initial gauge pressure on the furfural yield at 250, 275 and 225 °C are shown in Figures 4.15, 4.16 and 4.17, respectively. The results show that the furfural yield increased as the initial gauge pressure was increased. Also, the results show that the highest yield was obtained with γ–alumina. Figures 4.16 and 4.17 show the effect of pressure on the furfural yield at 275 and 225 °C respectively using 1 g (or W/WA₀ of 0.1) of γ–alumina. The furfural yields at 225 and 275 °C were lower than those at 250 °C whereas the trends were similar.

On the other hand, the effect of initial gauge pressure on the total gas yield is shown in Figures 4.18, 4.19 and 4.20 at 250, 275 and 225 °C respectively. In general, the total gas yield decreases as the pressure increases. The highest gas yield was obtained with H-ZSM-5 at 250 °C; however, γ–alumina was used at 225 and 275 °C for comparison purposes for furfural yield. Clearly, increasing the initial gauge pressure leads to an increase in the furfural yield due to increasing the condensation of the gases to form more liquid products (Harry, 2012).
**Figure 4.15:** The effect of the initial gauge pressure of the reactor on the furfural yield at retention reaction time 0 min, 1g catalyst, 10 wt % flax straw, and temperature of 250 °C.

**Figure 4.16:** The effect of the initial gauge pressure of the reactor on the furfural yield at retention reaction time 0 min, 1g γ-alumina 10 wt % flax straw, and temperature of 275 °C.
Figure 4.17: The effect of the initial gauge pressure of the reactor on the furfural yield at retention reaction time 0 min, 1g γ-alumina, 10 wt % flax straw, and temperature of 225 °C.
Figure 4.18: The effect of the initial gauge pressure of the reactor on the total gas yield at retention reaction time 0 min, 1g of catalyst, W/WA₀ of 0.1, 10 wt% of flax straw, and temperature of 250 °C.

Figure 4.19: The effect of the initial gauge pressure of the reactor on the total gas yield at retention time of 0 min, 1g γ-alumina, W/WA₀ of 0.1, 10 wt% flax straw, and temperature of 275 °C.
Figure 4.20: The effect of the initial gauge pressure of the reactor on the gas yield at retention time of 0 min, 1g γ-alumina, W/WA₀ of 0.1, 10 wt % of flax straw, and temperature of 225 °C.
In summary, \(\gamma\)-alumina showed the best performance in furfural production compared with the other two acid catalysts (H-ZSM-5 and silica-alumina) for all of the experimental parameters (temperature, pressure, retention time and weight of catalysts (W/W\(_A_0\))) considered. The highest yield of furfural was obtained with \(\gamma\)-alumina because \(\gamma\)-alumina has more Lewis acid sites compared with H-ZSM-5 and silica-alumina. The production of furfural from lignocellulosic biomass is mainly formed by the dehydration of pentose (Runge and Zhang, 2012). This process needs more protons to be available which can be provided through the dissociation of water at subcritical condition. The Lewis acid sites on the \(\gamma\)-alumina work as electron acceptors and attract the hydroxyl ions that are produced from water and that will increase the dissociation rate of water to produce more protons to complete the dehydration process of pentose to form more of furfural yields.

**4.3. THE EFFECT OF THE ACID SITES ON THE FURFURAL AND GAS YIELDS:**

Table 4.3 shows the ratio of Lewis to Brønsted acid sites as well as the number of Lewis acid sites in the three catalysts: H-ZSM-5, \(\gamma\)-alumina and silica-alumina. The acid sites labelled as (L) for Lewis acid sites and (B) for Brønsted acid sites. The values in Table 4.3 were obtained from the literature (Amin and Kusmiyati, 2004; Danuthai et al., 2009; Weingarten et al., 2011). The trend for the three acid catalysts according to L/B ratio was: \(\gamma\)-alumina > H-ZSM-5 > silica-alumina. The highest Lewis acid sites were obtained on \(\gamma\)-alumina as 0.257 mmol/g cat. Figure 4.21 indicates the performance of the three catalysts in furfural production at 250 °C based on the ratio of Lewis to Brønsted
acid sites. The highest performance was obtained with γ–alumina, which has the highest L/B ratio while silica-alumina gave the poorest performance in furfural production. Moreover, Figure 4.22 Shows the performance of the three catalysts at 250 °C based on the total gas yield. The figure shows that the lowest gas yield was obtained with γ-alumina, which means that γ–alumina increases the rate of the ionic pathway to form more furfural rather than selecting the free radical pathway.

**Table 4.3:** The ratio of Lewis to Brønsted acid sites of the three solid acid catalysts used in this study

<table>
<thead>
<tr>
<th>catalyst</th>
<th>Lewis/Brønsted acid site ratio (L/B)</th>
<th>Lewis sites mmol/g</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>silica-alumina</td>
<td>0.265</td>
<td>0.09</td>
<td>Weingarten et al., 2011</td>
</tr>
<tr>
<td>H-ZSM-5</td>
<td>0.63</td>
<td>0.037</td>
<td>Amin and Kusmiyati, 2004; Danuthai et al., 2009</td>
</tr>
<tr>
<td>γ–alumina</td>
<td>1.493</td>
<td>0.257</td>
<td>Weingarten et al., 2011</td>
</tr>
</tbody>
</table>
Figure 4.21: Comparison of the three catalysts based on the ratio of Lewis to Brønsted acid sites for the furfural productions at 250 °C.

Figure 4.22: Comparison of the three catalysts based on the ratio of Lewis to Brønsted acid sites for the gas productions at 250 °C.
4.4 THE EFFECT OF THE ACIDITY STRENGTH ON FURFURAL YIELD:

The temperature programmed desorption of ammonia of the three catalysts was adopted from (Pathak, 2005). The temperature programmed desorption reflects the acidity strength of the catalyst. The higher temperature of desorption means the higher acidity strength and vise versa. The acid strength of the catalysts increased as follows: silica-alumina < H-ZSM-5 < γ–alumina. Figure 4.23 shows the effect of acid strength on furfural yield. The figure shows that furfural yield increases as the acid strength of the catalyst increases. The relationship between the furfural production and the acidity strength follows a somewhat linear relationship.

Figure 4.23: The effect of the acid strength of the three catalysts on the furfural yield.
4.5 KINETIC STUDY OF THE CATALYTIC SUBCRITICAL HYDROTHERMAL GASIFICATION OF FLAX STRAW

4.5.1 Carbon Conversion and Reaction Rate

A total of twelve experiments were performed at the optimum weight of \( \gamma \)-alumina (1 g) per fixed weight of flax straw (10 g) in suspension (i.e. \( W/W_{A0} = 0.1 \)). Three temperatures were used (i.e. 225, 275 and 325 \(^\circ\)C) at four different residence time (0, 60, 90 and 120 min). The initial gauge pressure was kept autogenous in all the twelve experiments. The conversion was calculated as the difference in the carbon content of the flax straw and the carbon content in the char samples at the end of the experiments divided by the carbon content in the flax straw. The carbon content in the char samples was analysed by Loring Laboratories (Calgary, AB, Canada). The carbon conversion was calculated with the following equation:

\[
X_A = \frac{W_{ci} - W_c}{W_{ci}}
\]  (4.1)

where: \( X_A \) = the carbon conversion of the flax straw

\( W_{ci} \) = the weight of carbon in the flax straw.

\( W_c \) = the weight of carbon in the char samples in the end of the reaction.

The residence time was considered as the time to reach the temperature added to the time of holding the temperature before starting the cooling step. The carbon conversion was plotted versus the residence time at the three temperatures (225, 275 and 325 \(^\circ\)C) and the curves were fitted using MATHLAB SIMULINK software. The carbon conversions at
225, 275 and 325 °C are shown in Figures 4.24, 4.25 and 4.26, respectively while Figure 4.27 combines the carbon conversion of all the three temperatures in one drawing.

Figure 4.24: Carbon conversion of 10wt% flax straw at 225 °C, autogenous, and 1 g γ-alumina, W/W_{A0} of 0.1. (R^2 = 0.995)
Figure 4.25: Carbon conversion of 10wt% flax straw at 275 °C, autogenous, and 1 g γ-alumina, W/W$_{A0}$ of 0.1 (R$^2 = 0.993$).
Figure 4.26: Carbon conversion of 10wt% flax straw at 325 °C, autogenous, and `1 g γ-alumina, W/W\textsubscript{A0} of 0.1 (R\textsuperscript{2} = 0.992).
Figure 4.27: Carbon conversion of 10wt% flax straw at 225, 275, 325 °C, autogenous, and 1 g γ-alumina, W/W<sub>A0</sub> of 0.1.
The reaction rate was calculated as the slope \((dX_A/dt)\) of the curve at each point. The highest carbon conversion of 66\% was obtained at 325 °C, which is higher than the conversion of 40\% obtained in the non-catalytic study by Harry (2012).

**Table 4.4**: Experimental kinetic data

<table>
<thead>
<tr>
<th>Experimental rate ((dX_A/dt)) (mol/g*min)</th>
<th>Temperature (K)</th>
<th>Carbon conversion ((X_C))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0033</td>
<td>498</td>
<td>0.358</td>
</tr>
<tr>
<td>0.0021</td>
<td>498</td>
<td>0.500</td>
</tr>
<tr>
<td>0.0015</td>
<td>498</td>
<td>0.557</td>
</tr>
<tr>
<td>0.0009</td>
<td>498</td>
<td>0.564</td>
</tr>
<tr>
<td>0.0034</td>
<td>548</td>
<td>0.407</td>
</tr>
<tr>
<td>0.0022</td>
<td>548</td>
<td>0.553</td>
</tr>
<tr>
<td>0.0016</td>
<td>548</td>
<td>0.608</td>
</tr>
<tr>
<td>0.001</td>
<td>548</td>
<td>0.606</td>
</tr>
<tr>
<td>0.0035</td>
<td>598</td>
<td>0.451</td>
</tr>
<tr>
<td>0.0023</td>
<td>598</td>
<td>0.600</td>
</tr>
<tr>
<td>0.0017</td>
<td>598</td>
<td>0.663</td>
</tr>
<tr>
<td>0.0011</td>
<td>598</td>
<td>0.663</td>
</tr>
</tbody>
</table>
4.5.2. Kinetic Study on The Catalytic Hydrothermal Gasification of Flax Straw

Using Power Law Model

The kinetic modeling was performed using an empirical model to fit the kinetic data. The reaction rate for the batch reactor is (Levenspiel, 1999):

\[-r_A = \frac{dX_A}{dt} = k (1 - X_A)^n\]  (4.2)

The rate constant can be written as

\[k = A e^{-E/RT}\]  (4.3)

where

- \(A\) = pre exponential factor (or collision factor)
- \(E\) = activation energy (J/mol)
- \(T\) = reaction temperature (K)
- \(R\) = gas constant (8.314 J/mol K)

The final rate equation can be obtained by the substitution of the rate parameters in the rate equation

\[dX_A/dt = A e^{-E/RT} (1 - X_A)^n\]  (4.4)
4.5.3. Estimates of the Values of the Kinetic Parameters

The empirical kinetic model was used to fit the kinetic data of the reaction and the carbon conversion of flax straw at different temperatures. The kinetic parameters (A, E and n) were regressed using the NLREG software. The estimates of the parameters of the rate model are shown in Table 4.5. The effect of using γ–alumina in this study was observed by obtaining a smaller activation energy (9463.5 J/mol) compared with (27969.63 J/mol) obtained in the non-catalytic study (Harry, 2012). The experimental data was in a good agreement with the predicted data from the rate model with $R^2 = 0.9510$. The predicted rate values were obtained by substituting the kinetic parameters in the rate model. The experimental rate values and the predicted rate values were compared using a parity plot (Figure 4.28) and also by calculating the average absolute deviation, which gave a value of 8.6 %. The average absolute deviation was calculated using the following expression:

$$\text{AAD\%} = \frac{\text{Experimental rate} - \text{predicted rate}}{\text{Experimental rate}} \times 100$$ (4.5)

The parity plot shows good agreement between the experimental rate and the predicted rate values. The final rate model after substituting the kinetic parameters is as follows:

$$-r_A = \frac{dX_A}{dt} = 7.038 \times 10^{-2} e^{-\frac{9463.5}{R*T}} (1 - X_A)^2$$ (4.6)
Table 4.5: Estimates of the Parameters of the Rate Model

<table>
<thead>
<tr>
<th></th>
<th>E (J/mol)</th>
<th>n</th>
<th>R^2</th>
<th>AAD%</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>7.038 * 10^-2</td>
<td>9463.5</td>
<td>2</td>
<td>0.9510</td>
</tr>
</tbody>
</table>
Figure 4.28: Parity plot of experimental rate versus predicted rate
5.1 CONCLUSIONS

This project was focused on the hydrothermal gasification of flax straw using three solid acid catalysts (γ-alumina, H-ZSM-5 and silica-alumina). Furfural was the target product because of its importance in the industrial sector. The effects of the experimental parameters (temperature, pressure, residence time weight of catalyst and \( \text{W/WA}_0 \)) were investigated in this study. According to the results of this study, γ-alumina showed the highest yield of furfural compared with H-ZSM-5 and silica-alumina. As the temperature increases, furfural yields decreased whereas the yields of phenol and gas increased for all the three catalysts. The optimum temperature for producing furfural with γ-alumina was 250 °C, which is lower than the optimum temperature of 275 °C in the case of the non-catalytic study (Harry, 2012). An increase in the residence time led to a decrease in furfural yield but an increase in gas yield. Moreover, furfural yield increased with an increase in the initial gauge pressure while the gas yield decreased.

The optimum weight of catalyst which gave the highest yield of furfural was 1 g cat/10 g flax straw (i.e. \( \text{W/WA}_0 = 0.1 \)) for all of the three catalysts. Increasing the weight of catalyst over 1 g or \( \text{W/WA}_0 \) over 0.1 decreased the furfural yield while increasing gas yield for all the three catalysts. The carbon conversion in this study reached 66%, which is higher than the carbon conversion obtained by the non-catalytic study of 40% by Harry (2012). Kinetic modeling was performed in this study using an empirical rate model. The rate equation obtained was form:
-r_A = \frac{dX_A}{dt} = 7.038 \times 10^{-2} \ e^{-\frac{9463.5}{R \cdot T}} (1 - X_A)^2, \text{ with an activation energy of 9463.5 J/mol and a reaction order of 2.} \text{ The final optimum conditions for furfural production by hydrothermal gasification of flax straw in subcritical water are 250 °C, 0 min of residence time after it has reached the desired temperature, 0.1 g γ-alumina/g flax straw and a pressure of 60 bar.}
5.2 RECOMMENDATIONS

The recommendations that can be obtained from this study are summarized:

- There is need to screen more solid acid catalysts with more Lewis acid sites for investigating their performance on furfural production.
- There is also need to perform a long term stability test for the catalysts.
- There is a need to perform smaller residence times tests such as 1 or 2 min to know their effect on the furfural production.
- The effect of the agitation speed should be determined in future studies.
- It is recommended that a kinetic model be developed using LHHW and/or ER approaches in order to be able to interpret the intermediate steps during the formation of furfural from flax straw.
REFERENCES


(2013). Direct conversion of rice straw catalyzed by solid acid supported-Pt
catalyst using in situ H₂ by ethanol steam reforming. Fuel, 1-5.

HY Zeolite for Preparing Heterogeneous Cu Catalyst, Appl. Catal. A: General 202,
107-115.
THE CALCULATION OF THE LIQUID AND GAS YIELDS

The formula used to calculate the yield of the component is:

\[
\text{Yield of the component} = \frac{\text{mole or gram of the component}}{\text{gram of the used flax straw}}
\]

Where: this component could be the gas or the liquid.

LIQUID YIELD

The injection of the liquid sample in the GC-MS was performed using the same set of integration parameters being used previously by (Harry, 2012). The area of the liquid product was taken to find its concentration using the calibration curves. The calibration curves of furfural and phenol were taken from the thesis of the non-catalytic study made by our group member (Harry, 2012).

EXAMPLE OF LIQUID YIELD CALCULATION

If the liquid component concentration value is 0.197554 g/L and by converting it to be 0.197554 mg/ml so, water amount used here 90 ml equal to 90 mg.

By multiply the water value with concentration value as: 0.197554 mg/ml * 90 ml = 19.7799 mg.

In this study 10 g of flax straw is used so: 19.7799 mg / 10 g = 1.77799 mg / g of the flax straw. Then changing the value of the component to g of the component / g of the flax straw.
Calibration curve of phenol (Harry, 2012)

Calibration curve of furfural (Harry, 2012)
GAS YIELD

The calculation of the gas yield is done by taking the fraction percent of the component from the GC chromatogram and multiply it by the volume flow rate. The determination of the component as mol of the component / g of the flax straw is by dividing it with the amount of the flax straw used in the experiment.

EXAMPLE OF GAS YIELD CALCULATION

For example as a basis time = 1 min and if the volume percent of CO₂ taken as 56% and the volume flow rate of the gas = 468 cm³ /min. The volume fraction of the CO₂ = the mole fraction of CO₂ = 0.56 * 468 = 262.08 cm³/min = 262.08 mole/min.

If the flax straw amount used = 10 g so the yield of the CO₂ = 262.08 mole / 10 g flax straw = 26.208 mole / g flax straw. The total gas yield is taking after that as the summation of the gas yield of all gas.
CALCULATION OF CARBON CONVERSION

The carbon conversion of the flax straw ($X_c$) is determined by using CHNSO analysis of the carbon content in the original flax straw and in the char sample in the end of the reaction.

$$(X_c) = \frac{W_{ci} - W_c}{W_{ci}}$$

Where:

$X_c$ : is the carbon conversion.

$W_{ci}$ : is the weight of the carbon in the flax straw.

$W_c$ : is the weight of the carbon in the char in the end of the reaction.

EXAMPLE OF CALCULATION :

Flax straw used is 10 g with carbon fraction of 0.481

$W_{ci} = 10 \times 0.481 = 4.81$ g

For example char sample of 2.8 g with carbon fraction of 0.56

$W_c = 2.8 \times 0.56 = 1.6$ g

$$(X_c) = \frac{4.81 - 1.6}{4.81} = 0.66$$
APPENDIX (B)

• CALCULATION OF REACTION RATES

The rate of the reaction is calculated by taking the differentiation of the fitness equation of the parabolic curve of the conversion.

Example:

At 225 °C:

Y = \(-1.2 * 10^{-5}X^2 + 0.0033X + 0.36\)

By taking the differentiation of the equation we will get the slope which is equal to the rate.

\[ r_A = \frac{dX}{dt} = \frac{dy}{dx} = 2 (-1.2 * 10^{-5}) * X + 0.0033 \]

where: X is the retention time of the reaction used and Y is the carbon conversion.
APPENDIX (C)

- THE CODE OF NLREG SOFTWARE FOR DETERMINATION OF KINETIC PARAMETERS

The results found in the Table obtained by the regression of the parameters of A, E, n by using this formula:

\[
\begin{align*}
    r_A &= \frac{dX_A}{dt} = k(1 - X_A)^n \\
    -r_A &= \frac{dX_A}{dt} = Ae^{(-E/RT)} (1 - X_A)^n
\end{align*}
\]

The following code is used to determine the kinetic parameters:

Title "Rate Model of Catalytic Hydrothermal Gasification of Flax Straw";

variable r, T, X_A;

parameter A, E, n;

function r= A*exp(-E/(8.314*T))*(1-X_A)^n;

plot;

where:

R= 8.314

X_A: is the carbon conversion.

\[
\begin{align*}
    r &= \frac{dX_A}{dt}
\end{align*}
\]

The regression using NLREG is shown in the next page:
Rate Model of Catalytic Hydrothermal Gasification of Flax Straw

```
Title "Rate Model of Catalytic Hydrothermal Gasification of Flax Straw";

variable r, T, XA;
	parameter a, e, n;

function r = A*exp(-E/(8.314*T))*(1-XA)^n;

plot;

data;

Beginning computation...
Stopped due to Relative function convergence.

---- Final Results ----

NLREG version 6.5
Copyright (c) 1992-2006 Phillip H. Sherrod.

Rate Model of Catalytic Hydrothermal Gasification of Flax Straw

Number of observations = 10
Maximum allowed number of iterations = 500
Convergence tolerance factor = 1.000000E-010
Stopped due to Relative function convergence.
Number of iterations performed = 24
Final sum of squared deviations = 3.2143902E-097
Final sum of deviations = -9.0543792E-006
Standard error of estimate = 0.000215386
Average deviation = 0.000142140
Maximum deviation for any observation = 0.000359252
Proportion of variance explained (R^2) = 0.9910( 99.10%)
Adjusted coefficient of multiple determination (R^2) = 0.9369 (93.69%)
Durbin-Watson test for autocorrelation = 1.616
Analysis completed 10-Oct-2013 19:07. Runtine = 0.14 seconds.

---- Descriptive Statistics for Variables ----

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<th>Variable</th>
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<th>Mean Value</th>
<th>Standard Dev.</th>
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---- Calculated Parameter Values ----

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<th>Prob(t)</th>
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---- Analysis of Variance ----

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